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| 13. ABSTRACT (Maximum 200 words) The purpose of the research was to determine the feasibility of developing electronic sensors for measuring various properties of cold-region soils. Research was performed to produce prototype sensors with fill solutions that would allow for operation in the temperature ranges of interest. It would appear that further research will result in the ability to evaluate the effectiveness of bioremediation methods. The need for performing in-situ bioremediation is becoming increasingly apparent in the on-going battle to clean up contaminated soils from a man-power and litigation perspective. Developing the tools for analyzing the success of bioremediation will have a global commercial impact. | | | |
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TOPIC: A94-091 TITLE: In-Situ Electronic Sensors to Determine Analytes in Cold-Regions Soils.

Phase I Final Report

Introduction

The ability of performing in-situ bioremediation or natural attenuation is becoming increasingly apparent in the on-going battle to clean up contaminated soils. This is a far-reaching problem ranging from Super Fund sites, government research labs, military bases, industrial petro-chemical plants and plating shops -- all the way down to individuals polluting their neighbors potable well water by over-fertilizing their crops or lawns. It has become quite obvious that the removal or excavation of the land for treatment or disposal at a designated, approved dump-site is unreasonable and cost prohibitive from both a man-power and litigation standpoint. This will only continue to become worse as the abilities to locate these sites improve. The acceptance that it took many years to pollute the soils and that it will take many more years to correct the situation is essential from a scientific and more importantly an economic perspective. In-situ bioremediation appears to hold tremendous promise at this time.

The problem is exacerbated in cold regions due to the difficulty of digging up frozen tundra and the lack of knowledge of microbial migration patterns -- indigenous or otherwise. Therefore, it is paramount to have the capability of determining the correlation between CO_2 , NH_3 , NH_4^+ , NO_3^- , and O_2 as they pertain to effective in-situ bioremediation of the contaminated soils in a three-dimensional manner.

This brings us to the primary problem to be addressed by this SBIR request -- the need for development of specific ion sensors that can work reliably in sub-freezing environments to allow unmanned dataloggers to accumulate data on a downloaded or real-time basis. The technology for the sensors is already basically in place -- but there would be some research required to allow the measurements to be taken in sub-freezing environments. This would involve re-designing the reference side of the electrode (half-cell) to be rugged enough to survive the conditions imposed upon it while also determining whether the changes would compromise the necessary data. The ability to interface to the dataloggers simultaneously with several variables would also require electronic isolation techniques to prevent problems associated to ground-loops which could prove to be substantial in colder soils and groundwater of very low conductivity. Again many isolation themes are very adaptable to these situations -- but some research would be necessary to determine what would be optimal from a power and cost standpoint. This becomes all the more important due to the necessity to allow for unmanned, self-powered datalogging. Power requirements have to be kept to a minimum. Another problem that presents itself is the ability to miniaturize the sensor/transmitter in such a manner as to enable insertion into very small wells which

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odes

or

would decrease the cost of application. Surface mount electronics are quite capable and practical in this instance.

The benefits would be broad-reaching with commercial applications from citizen to global in scale.

Phase I Technical Objectives:

1. Evaluate existing technology to allow for an expedient and economical solution to the problem of cold-region monitoring of groundwater and/or gases as specified.
2. Determine and define any areas that may present difficulties.
3. Develop a reference fill solution for each of the ions of interest (CO_2 , NH_3 , NH_4^+ , NO_3^- and O_2) that will resist freezing while still yielding useable data.
4. Develop prototypes of combination sensor/transmitters to allow for in-situ cold-region data gathering of the above parameters.

Materials and Methods:

Equipment:

Cryostat Tissue-Tek II Refrigeration Unit

Use: For testing to -15°C of electronics, standards and sensors.

Analogic DP100 Digital Voltmeter

Use: For making 5-1/2 digit readings for testing of electronics linearity and drift.

Fluke 8022B Digital Voltmeter

Use: For resolving 0.1mV input readings for testing of electronics linearity and drift.

Uniloc Model 213 mV Simulator

Use: To provide a low output impedance mV source for testing of electronics linearity and drift.

Corning Model 125 Specific Ion Meter

Use: Measuring mV outputs of various sensors. All readings performed through a unity gain preamp with better than $10^{12} \Omega$'s input impedance and less than 1 pico-amp leakage current. Offset voltage and gain zeroed and spanned with preamp in series.

Sartorius BP110S Scale

Use: For measuring chemicals. 0.1 mg resolution.

Lauda K20 Temperature Controlled Bath

Use: For 25 °C tests.

Sensor/Transmitters:

Phionics STx Series

CRREL CO₂, Serial No: 5120411

CRREL NH₃, Serial No: 5120415

CRREL NH₄, Serial No: 5120412

CRREL NO₃, Serial No: 5120414

CRREL O₂, Serial No: 5120413

Chemicals and standards:

CO2STD1: 100 ppm CO₂ standard

Prepared: 0.191 grams NaHCO₃ filled to 1 liter with H₂O.

CO2STD2: 10 ppm CO₂ standard

Prepared: Serial Dilution 100ml CO2STD1 filled to 1 Liter with H₂O.

CO2BUFF1: 1M Sodium Citrate Dihydrate

Prepared: 294 grams Na₃C₆H₅O₇·2H₂O filled to 1 Liter with H₂O.

CO2REF1: Internal Fill Solution

Per 100 ml: 0.8g Sodium Bicarbonate (NaHCO₃).

CO2REF2: Internal Fill Solution

Per 100 ml: 0.8g Sodium Bicarbonate, 40 ml Glycerol (99%)

10 ppm CO₂ Reading:

Place 100 ml CO2STD2 in a tall beaker on a magnetic stirrer, add 10 ml CO2BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

100 ppm CO₂ Reading:

Place 100 ml CO2STD1 in a tall beaker on a magnetic stirrer, add 10 ml CO2BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

NH3STD1: 100 ppm NH₃ as N standard

Prepared: 0.382 grams NH₄Cl filled to 1 liter with H₂O.

NH3STD2: 10 ppm NH₃ as N standard

Prepared: Serial Dilution 100ml NH3STD1 filled to 1 Liter with H₂O.

NH3BUFF1: 10M Sodium Hydroxide

Prepared: 400 grams NaOH filled to 1 Liter with H₂O.

NH3REF1: Internal Fill Solution

Per 100 ml: 0.53g Ammonium Chloride (NH₄Cl)

NH3REF2: Internal Fill Solution

Per 100 ml: 0.53g Ammonium Chloride, 40 ml Glycerol (99%)

10 ppm NH₃ Reading:

Place 100 ml NH3STD2 in a tall beaker on a magnetic stirrer, add 1 ml NH3BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

100 ppm NH₃ Reading:

Place 100 ml NH3STD1 in a tall beaker on a magnetic stirrer, add 1 ml NH3BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

NH4STD1: 100 ppm NH₄⁺ standard

Prepared: 0.297 grams NH₄Cl filled to 1 liter with H₂O.

NH4STD2: 10 ppm NH₄⁺ standard

Prepared: Serial Dilution 100ml NH4STD1 filled to 1 Liter with H₂O.

NH4BUFF1: 5M Sodium Chloride

Prepared: 292 grams NaCl filled to 1 Liter with H₂O.

NH4REF1: Internal Fill Solution

Per 100 ml: 0.58g Sodium Chloride (NaCl)

NH4REF2: Internal Fill Solution

Per 100 ml: 0.58g Sodium Chloride, 40 ml Glycerol (99%)

10 ppm NH_4^+ Reading:

Place 100 ml NH4STD2 in a tall beaker on a magnetic stirrer, add 2 ml NH4BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

100 ppm NH_4^+ Reading:

Place 100 ml NH4STD1 in a tall beaker on a magnetic stirrer, add 2 ml NH4BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

NO3STD1: 100 ppm NO_3^- standard

Prepared: 0.137 grams NaNO_3 filled to 1 liter with H_2O .

NO3STD2: 10 ppm NO_3^- standard

Prepared: Serial Dilution 100ml NO3STD1 filled to 1 Liter with H_2O .

NO3BUFF1: 2M Sodium Citrate Dihydrate

Prepared: 264 grams $(\text{NH}_4)_2\text{SO}_4$ filled to 1 Liter with H_2O .

NO3REF1: Internal Fill Solution

Per 100 ml: 0.13g Ammonium Sulfate $((\text{NH}_4)_2\text{SO}_4)$

NO3REF2: Internal Fill Solution

Per 100 ml: 0.13g Ammonium Sulfate, 40 ml Glycerol (99%)

10 ppm NO_3^- Reading:

Place 100 ml NO3STD2 in a tall beaker on a magnetic stirrer, add 2 ml NO3BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

100 ppm NO₃⁻ Reading:

Place 100 ml NO3STD1 in a tall beaker on a magnetic stirrer, add 2 ml NO3BUFF1 and stir at constant rate. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6, 7 at end of section.

O2REF1: Internal Fill Solution

Per 100 ml: 0.2g Sodium Hydroxide (NaOH)

O2REF2: Internal Fill Solution

Per 100 ml: 0.2g Sodium Hydroxide, 40 ml Glycerol (99%)

Lo O₂ Reading:

Purge O₂ from H₂O using N₂. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6 at end of section.

Hi O₂ Reading:

Saturate H₂O with air using an air pump and porous stone. Approximates 8.38 ppm O₂ at 25 °C and 760 mm. Lower electrode into solution until SS housing contacts solution. After the reading has stabilized, record the mV value. See Note 1, 2, 3, 4, 5, 6 at end of section.

Methods:

Internal Fill Solution Freezing Tests

How performed: Samples were placed in weighing boats in the Cryostat at -15 °C. Samples were allowed to stabilize for one hour or until there were obvious indications that the materials had frozen. 'Passed' indicates sample withstood exposure without freezing. 'Failed' indicates sample froze as a consequence of exposure.

Why performed: To determine if xxxREF2 demonstrated the ability to go below the -10 °C objective of the project.

Internal Fill Solution Operational Tests

How performed: Initial tests of sensors were made at 25 °C in temperature controlled bath at two points using chemicals and standards

as described previously with an internal fill solution designated as xxxREF1 (substitute ion of interest for xxx – such as CO2REF1 for CO₂, etc.). Secondary tests of sensors were made at 25 °C in temperature controlled bath at two points using chemicals and standards as described previously with an internal fill solution designated as xxxREF2.

Why performed: To determine if chemistries had been altered in such a way as to make sensors respond in a non-Nernstian or deleterious manner – significant changes in offsets or spans.

Electronics Temperature Tests

How performed: Electronics were placed in six mil plastic bags inside of Cryostat to prevent effects of condensation. Input was external to Cryostat and where applicable power was also provided externally to prevent temperature effects attributable to anything other than the circuit under test. In the case of the battery powered units, batteries were inside of Cryostat to verify that they maintained functionality throughout temperature ranges. Temperatures were allowed to stabilize for thirty minutes after temperature had been reached before readings were taken. Current readings were taken with the Analogic DVM in the current mode. Readings of mV inputs were made with the Fluke DVM on the mV range. Readings of mV outputs were made with the Analogic DVM on the mV range. Electronics consisted of existing proprietary designs with modifications made as necessary to allow for operation to -10 °C.

Why performed: To determine if electronics could attain -10 °C specification without any undue compromises.

Note 1: Always rinse electrodes with distilled water between readings, minimizing cross-contamination of solutions.

Note 2: DVM (digital voltmeter) should have negative lead (usually black) connected to the sensor black wire and the positive lead (usually red) connected to the sensor red wire. Note input impedance of measuring device.

Note 3: There is a one megohm resistor in series with the output of the transmitter – this is to prevent the premature failure of the unit (they should last approximately two and a half years) due to battery drain by inadvertently shorting the output wires together. Therefore when making measurements with a digital voltmeter or datalogger the input impedance must be factored in. For a typical input impedance of 10 megohms, and an output of 182 mV:

$$(10 \text{ megohm} / (10 \text{ megohm} + 1 \text{ megohm})) 182 \text{ mV} = 165.4 \text{ mV}$$

This would result in a nine percent error. During our testing we took all output data through another high impedance preamp that was not short-circuit protected (output source impedance less than 10 ohms which yields $(10M/(10M + 10 \text{ ohms})) 182 \text{ mV} = 181.9998 \text{ mV}$ which is negligible error) and that was corrected electronically for voltage offset – resulting in good confidence in the integrity of our data.

Note 4: The sensors have a differential input which allows for discrimination of small signals from noise which is inherent in high output impedance electro-chemical sensors. A differential input requires a solution ground to reference the front-ends of the reference and measurement cell to a common point for the cancellation of the noise signal. On our units we use the Stainless Steel sensor body as this third contact with the solution. This contact *must* be made with the groundwater or sample for any meaningful data to be obtained.

Note 5: All samples and standards should be made at the same temperature for accurate measurement. A difference of 1 °C in temperature will result in approximately a 2% error.

Note 6: The ratio of surface area to volume in the container should be kept at a minimum. Beakers containing the samples or standard should be kept covered between measurements.

Note 7: Add the xxxBUFF1 just before measurement.

Phase I Results:

Internal Fill Solution Freezing Tests

| Temp °C | CO2REF1 | NH3REF1 | NH4REF1 | NO3REF1 | O2REF1 |
|---------|---------|---------|---------|---------|--------|
| -15 | Failed | Failed | Failed | Failed | Failed |
| Temp °C | CO2REF2 | NH3REF2 | NH4REF2 | NO3REF2 | O2REF2 |
| -15 | Passed | Passed | Passed | Passed | Passed |

Internal Fill Solution Operational Tests (all readings in mV)

CO₂:

| | | |
|----------|--------|---------|
| Standard | CO2REF | CO2REF2 |
| 10 ppm | -72 | -78 |
| 100 ppm | -19 | -26 |

NH₃:

| | | |
|----------|---------|---------|
| Standard | NH3REF1 | NH3REF2 |
| 10 ppm | -10 | -17 |
| 100 ppm | -63 | -72 |

NH₄⁺:

| | | |
|----------|---------|---------|
| Standard | NH4REF1 | NH4REF2 |
| 10 ppm | -5 | -12 |
| 100 ppm | 50 | 45 |

NO₃⁻:

| | | |
|----------|---------|---------|
| Standard | NO3REF1 | NO3REF2 |
| 10 ppm | 120 | 118 |
| 100 ppm | 64 | 62 |

O₂:

| | | |
|----------|--------|--------|
| Standard | O2REF1 | O2REF2 |
| Lo | 549 | 492 |
| Hi | 584 | 520 |

Electronics Temperature Tests

Self-Powered Unity Gain Circuit

| Temp °C | V _{N1} (mV) | V _{OUT1} (mV) | V _{N1} (mV) | V _{OUT1} (mV) | V _{N1} (mV) | V _{OUT1} (mV) |
|---------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|
| 22 | -199.8 | -199.6 | 000.0 | 000.2 | 199.7 | 199.9 |
| 1 | | -199.5 | | 000.3 | | 200.0 |
| -16 | | -199.4 | | 000.3 | | 200.1 |

2-Wire 4-20 ma Circuit

| Temp °C | V _{N1} (mV) | I _{OUT1} (ma) | V _{N1} (mV) | I _{OUT1} (ma) | V _{N1} (mV) | I _{OUT1} (ma) |
|---------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|
| 24 | -199.8 | 4.006 | 000.0 | 11.998 | 199.7 | 19.990 |
| 0 | | 4.002 | | 11.994 | | 19.987 |
| -15 | | 3.990 | | 11.983 | | 19.977 |

Summary:

Phase I was basically a feasibility, problem gathering, electro-mechanical program. We wanted to obtain gross data in a timely manner that would let us know quickly whether we were pursuing a proper direction with respect to each ion without concerning ourselves with the optimum accuracies that are obtainable if all variables are taken into account (such as interference ions, chemistries, temperature changes, pressure, etc.). We have every expectation that normal accuracies can be obtained once the electro-mechanical and basic electrode needs are addressed. In this vein, a great deal of the program was spent confirming that the electronics and the mechanical design were properly in place and researching the existing technologies for the sensors. The remaining twenty-five percent of the time was used performing several quick experiments to verify freezing point depression of the reference solutions and observing any deleterious effects that may have presented themselves when used in combination with the intended sensor.

Electronics:

We developed two complete approaches electronically to the transmitter aspect of the experiment that succeed to -10 °C. One approach is a self-powered differential amplifier unit that will address the problems of small differences in ground potentials that would commonly be found at most sites, and the other is a combination of galvanically and optically isolated, two-wire transmitter (4-20 milliamp) that addresses the problems of large ground potentials that may be found around manufacturing plants with large horsepower electrical equipment. The two-wire approach has the advantage of allowing long runs of cable back to the datalogger with minimal loss of signal and low noise pick-up at the expense of more operating current which can be a factor in battery operated applications. The units that we will be sending to CRREL will be the micropower self-powered units which we feel will have the widest appeal for working with the majority of dataloggers commercially available. We also gravitated to the self powered units due to the simplicity of data gathering – these are unity gain differential input units that allow us to make experimental observations without the need for introducing another source of error that could present itself during the scaling of the data. Therefore when we see an 11 mV change we know that it is an 11 mV change

instead of confusing the issue by determining that a 0.880 ma change on a 4-20 ma transmitter scaled for 200 mV full-scale is an equivalent measurement.

Note: There is a one megohm resistor in series with the output of the transmitter – this is to prevent the premature failure of the unit (they should last approximately two and a half years) due to battery drain by inadvertently shorting the output wires together. Therefore when making measurements with a digital voltmeter or datalogger the input impedance must be factored in. For a typical input impedance of 10 megohms, the aforementioned example of 11 mV would result in an apparent output of:

$$(10 \text{ megohm} / (10 \text{ megohm} + 1 \text{ megohm})) 11 \text{ mV} = 10 \text{ mV}$$

This would result in a nine percent error. During our testing we took all output data through another high impedance preamp that was not short-circuit protected (output source impedance less than 10 ohms which yields $(10\text{M} / (10\text{M} + 10 \text{ ohms})) 11 \text{ mV} = 10.99999 \text{ mV}$ which is negligible error) and that was corrected electronically for voltage offset – resulting in good confidence in the integrity of our data.

The units as provided to CRREL have a differential input which allows for discrimination of small signals from noise which is inherent in high output impedance electro-chemical sensors. The differential amplifier is a major reason why these type of sensors were able to migrate out of laboratories over the past thirty years and function in the more hostile industrial environments. A differential input does require a solution ground to reference the front-ends of the reference and measurement cell to a common point for the cancellation of the noise signal. On our units we use the Stainless Steel sensor body as this third contact with the solution. This contact must be made with the groundwater or sample for any meaningful data to be obtained. This implies that it may not work properly if sensing a gas not contained in a conductive medium such as water. This would require us to have a customer selectable option that would make the measurement single-ended with its apparent problems if they desire to measure gas only on the CO₂, NH₃, and O₂ versions of the sensors.

We tested the two versions of our existing proprietary electronic designs extensively from +25 °C down to -15 °C with both exhibiting less than 0.1 percent of full-scale total error after minor changes involving hand selection of a few components to allow for operation at the lower limit. This would be considered as commercially acceptable over the temperature spectrum. The electronics were tested in a Cryostat with the source voltage applied externally and monitored at ambient (approximately 20 °C) to be certain that any errors were a direct consequence of the electronics drift with temperature.

The electronics are quite stable and will not require any further work to be implemented in a future design beyond electro-mechanical packaging to allow for ease of manufacturing and testing.

Mechanical:

We implemented a mechanical design that allows for a quick assembly of the units that will be extremely adaptable to quick turn-around of future prototypes as well as useful in low-cost designs which we will make commercially available in the next couple of months. The design is of materials compatible with cold-region (and normal) operation of the sensor. The materials of construction are Delrin™ for the plastic bodies, 316 Stainless Steel for the housing and solution ground and Viton™ for the o-ring seals. The cable is PVC jacketed.

The mechanical design was tested at 100 psi pneumatically at room temperature and -15 °C and hydraulically at room temperature and -15 °C in a fifty-fifty solution of water and conventional antifreeze without any signs of seal failure around the sensor or the cable. The design was not tested during this phase with 'live' electrodes for fear of destroying the electrodes. We had accidentally destroyed several electrodes at a previous time due to some problems regarding incompatible coefficients of expansion during some temperature testing.

The mechanical package is basically a sound design at this time, however, we will want to implement it in a new package that will allow for better manufacturability and interchangeability at a later time to make it consistent with our standard product line which is currently on hold pending a few patent applications regarding the mechanical configuration.

Sensors:

We wanted to entertain off-the-shelf sensor technology that could minimize cost, appear to be successfully adaptable to the -10 °C specification, and could yield reasonable expectations for gathering useable data in-situ. This eliminated pumping and wet chemical analysis techniques. Though wet chemical techniques may result in a more reliable form of data gathering and open other avenues for preheating the samples – large scale implementation of the method would be prohibitive primarily from a cost standpoint and they have proven to be very maintenance intensive in analogous process control applications.

The most practical approach was to search for chemistries and techniques that could yield magnitudes of change as opposed to 0.1% accuracies which would be unrealistic in real world environments. With this in mind we acquired some sensors, modified some existing sensors and constructed a few of our own based on our experiences in the field.

We selected two technologies that best addressed the ions of interest with few or known compromises that can be allowed for – gas-sensing and ion exchange membrane. The CO₂ and NH₃ sensors are both gas-sensing in nature – using a gas

semi-permeable membrane that works on the principal of the internal chemistry being changed based on the migration of the respective gas ion (which in equilibrium will be in direct proportion to the partial pressure of the gas in solution) and resulting in a reversible reaction (pH) that correlates to the ion concentration which can then be sensed using an internal pH electrode and reference yielding a Nernstian response (approximately 59.2 mV/decade at 25 °C) [1]. O₂ is gas-sensing also, but relies on the reduction of O₂ at an inert electrode which creates the polarographic phenomena of a linearly increasing current proportional to the diffusion of ions once the voltage across the inert metal cathode (such as gold or platinum) and the silver anode is reached (between -0.05 to -0.9 volts – typically -0.5 to -0.7 is used). An extension of this is a galvanic method where the inert metal is replaced by lead at the cathode and a basic electrolyte is used to create a galvanic cell that can produce a sufficient potential to cause reduction of the O₂ without the necessity of an externally impressed voltage. The former O₂ sensor is generally referred to as polarographic and the latter is classified as galvanic for obvious reasons [2]. The NH₄⁺ and NO₃⁻ sensors are polymer membrane electrodes that work on the principle that ion exchange resins are embedded into an inert matrix (the polymer) and are designed to be selective for weak anions, strong anions, weak cations or strong cations. The species that they are not selective for will develop a potential with the internal sensing assembly.

CO₂: The CO₂ sensor has an extremely limited range of operability (tight pH tolerances which would critically limit its practical use in the field -- 4.8 to 5.2 pH) which would require being addressed in Phase II or in our own program when there is more time to do the basic compilation of existing techniques and currently manufactured sensors to find the approach that would best suit this application without resorting to wet chemistry methods, but we feel there is an excellent chance of modifying the current design with a second gas permeable membrane that can provide the necessary preconditioning (buffering) of the sample on the fly since it does work quite well in this range. In these pH tolerances the carbonate and bicarbonate forms are readily converted to CO₂ ($2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2$ and $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2$). However, CO₂ containing waters are typically on the acid side (approximately 4 pH) and would yield some useable results such as magnitude of change with twenty to thirty percent error. Quite often this could possibly be indicative of an activity of interest and any changes that may appear as the result of a stimulus, therefore providing useful feedback on a process. The CO₂ sensor will require some work being done on the internal glass electrode to allow it to go to -10 °C.

NH₃: The NH₃ sensor shares the same basic design as the CO₂ sensor in that it has a pH internal which will require some work as does the CO₂. A side issue regarding the NH₃ and the NH₄⁺ sensors is that a pH measurement may be desired to distinguish between ammonia and ammonium ions in that above 11 pH the prevalent form is NH₃ and below 7 pH the prevalent ion will be NH₄⁺. A pH measurement may be necessary to let the gatherer know when the data is valid and/or for what species [3].

NH₄⁺: The NH₄⁺ ion sensor works very well between 2 and 12 pH, but as noted above a separate pH reading may be desirable to distinguish ammonia and ammonium mixtures. This sensor as well as the NO₃⁻ simply require some work on the sensing half-cell to yield a useable cell.

NO₃⁻: The NO₃⁻ sensor also shares the need for manipulating the measuring side of the electrode to yield a complete cell capable of working down to -10 °C. Otherwise it shows relatively good results between 3 to 11 pH when similar interfering ions are not present.

O₂: The O₂ sensor is operable in its current format to -10 °C since it does not require any additional internal fill solution or special electrode modifications to function. For this reason it also was used for more of the tests since they were not catastrophic in their nature. The unit as shipped to CRREL is a galvanic style, but we have determined that the polarographic type will be what we incorporate into the next design because there are ways to electronically minimize the need for stirring or high flow rates (1.5 feet/sec) which is common in dissolved oxygen measurements due to the fact that the oxygen is consumed around the sensing membrane resulting in apparent lower readings [4].

Feasibility of Further Research:

With the exception of the O₂, more work will be required to lower the operability of the internal glasses and sensing elements that will require working more closely with the manufacturer of the internal glasses which takes time and iterations that can only be addressed in a longer program such as the two years suggested for Phase II. The development of the reference fill solutions was successful, but will require the further research on the internal glasses and sensing modules (mentioned above) to yield a truly functional sensor at -10 °C. However it would appear that a 40% glycerol addition in proportion to existing chemistries will yield operable sensors. Therefore it would appear to demonstrate a reasonable expectation of success in the Phase II program.

Where do we go from here? The following areas would be suggested for pursuit from the problems and questions that arose during the Phase I program.

1. Determine temperature curves for the various ions. These will typically follow the Nernstian response, however, they will need to be determined empirically to allow for real-world practical efficiencies at least at two points of concentration.
2. Determine Isopotential points of various electrodes. To allow for temperature correction, this point must be determined that allows for amplification from a point that introduces no errors or shifts. This would be a somewhat obvious by-product of step one above, and although this can be determined mathematically – the realities of dealing with real-world electrodes make empirical determination a necessity.

3. Determine gas curves for various electrodes. Obviously, this is the primary concern of the entire project. These would be determined across the temperature ranges from 20 to -10 °C. This would allow for interchangeability of sensors for field replacement. This would be accomplished using known standards.
4. Develop internal glasses for electrodes that can withstand -10 °C. We will specify to the glass manufacturers to make us several sensors at various fill solutions and test the degree of shift involved and/or degradation in measurement that may occur of a specific ion. The manufacturer of the various glasses can guide us in much of this endeavor, cutting down on the time required to find a responsive compromise of sensor responses.
5. Incorporate an independent temperature output in sensors and/or internal automatic temperature compensation for each sensor. We believe having an independent output for temperature can have some major advantages in the event that the isopotential point drifts as the electrode ages and degrades. If we develop procedures for determining the isopotential point in the field, and/or the change in the efficiency of the electrode, this would allow for correction by rewriting the equation in a spreadsheet for example without the necessity of scrapping the data (which may not be obtainable again in some remote sites).
6. Make the sensors field replaceable and/or easy to refill or rebuild. For ease of use and commercialization purposes the specific ion sensor/transmitters require the ability to be replaceable or to at least have their life extended due to their inherent high costs.
7. Do further research to determine if there are any technologies and/or techniques that can extend the practical operable range of the CO₂ sensor. This would require evaluating existing technologies to determine if something exists that does not have the pH range limitations currently exhibited. Introducing another buffering membrane layer may yield practical data. The CO₂ sensor currently would not be practical for the majority of field applications.

Further research would essentially be the shift from a feasibility, problem gathering, primarily electro-mechanical phase (as in Phase I) to a physical chemistry, problem solving, product development phase.

To eliminate confusion, cross-contamination and to allow for the most expedient development of useable sensors, the sensors would be approached one at a time, preferably developed in the following order -- O₂, NO₃⁻, NH₄⁺, NH₃, and CO₂. This would allow us to develop the sensors in the order that they appear to have the most commercial demand, while concurrently allowing the maximum amount of time for us to accumulate data in an effort to solve the problems with the CO₂. It also affords us the continuity of producing the manual while the problems and techniques are fresh in our minds for each respective parameter.

The program would start with the development of the dual output model that affords us an easy way to determine curves of interest. By making the electrodes field replaceable, it allows us to make electrodes that can be calibrated to some degree of interchangeability and/or it will allow us to make simple changes and iterations to the design without having to attack the entire mechanical package.

Concurrent with this, we would begin gathering data regarding the CO₂ solutions available to us and have the internal glasses manufactured to allow for evaluation on a continuing basis in an effort to eliminate any lags as each sensor is scheduled to be released.

[1] Durst, Richard A., *Ion Selective Electrodes*, National Bureau of Standards Special Publication 314, 1969, pp. 353-355.

[2] Sawyer, Clair N., *Chemistry for Sanitary Engineers*, McGraw-Hill, New York, pp. 274-277.

[3] Liptak, Bela G., Editor, *Environmental Engineers' Handbook*, Vol. 1, Chilton Book Co., Radnor, Pennsylvania, 1974, pp. 1311-1317.

[4] Liptak, Bela G., Editor, *Environmental Engineers' Handbook*, Vol. 1, Chilton Book Co., Radnor, Pennsylvania, 1974, pp. 610.